

Q&A Lecture 4

What happens if the electronic potential surfaces touch/intersect? How would the probability mass distribute between the states, and how would the coupling term look? I'm not sure how this would be different from then; they are just close, like in the example discussed in the lecture.

Actually, the situation does not change much qualitatively and the equations stay the same. In fact, the separation of energy states occurs in practice only for low-dimensional (one-dimensional "reaction" coordinate) situations and is known as an avoided crossing. In multidimensional cases, there is indeed a zero gap and the region corresponding to this is called a conical intersection. There are some phenomena (one in particular known as the Berry phase that has to do with an additional phase acquired by the coefficients based on the evolution equations as the intersection is crossed but is in practice very hard - if not impossible - to observe in experiments) that are specific to the conical intersections but the level of description provide in class is a very good first approximation also for this case.

Is the wavefunction completely defined for a certain R and I when the coefficients $c_i(R, H)$ are computed?

Yes, because of the property that once a basis is chosen, the representation via the coefficients is complete...and is not the wave function that is determined, but the state of the system of nuclei and electrons (the wave function would be the representation of this state in the coordinate basis for both sets).

Can we derive the conservation of the total population from the Franck-Condon principle?

No, but the Franck-Condon excitation will preserve the total population.

I am bit confused about R , R represented the location of nuclei, then during this week's lesson, R represented the distance between two nuclei?

In class, I tried to explain that R (by default the nuclear coordinates in the original equation) can be turned into any convenient coordinate representation - e.g. spherical, if we account for the variable transformations in the second derivative operator. In the example I draw on the board - which had to do with a diatomic, i.e. invariant system for rotations - the distance between the two nuclei was the convenient representation. The math is a bit long, but there is nothing conceptually new so I used the example directly.

So I got a little confused with the maths. So after imposing all these assumptions we still have a coupled channel equation with 2 unknowns (C and E), and since we only have one electronic state then that's the only equation we have. So how do we get the value of E to solve N2L?

In the Born-Oppenheimer approximation - which is the first step towards N2L - there is only one unknown and that is C . E is the ground state energy and - if we stay quantum - it needs to be computed as input information via the time-independent Schrödinger equation for the electronic Hamiltonian in the adiabatic basis. HOWEVER, importantly, when we take the step to say that the nuclear evolution is classical (N2L) we don't solve for C , but simply for the nuclear positions evolving in the potential determined by E .

I was unsure about the point of the discussion involving the "miniature version of Sara Bonella" who could talk to molecules and observe their behavior. Are there currently

experimental techniques capable of accurately tracking the motion and states of approximately 1,000 molecules over time?

The “mini-me” was invoked for a thought experiment to make the connection between the microscopic info provided by the coefficients and physical or chemical processes measurable in the system. I don't think that there is an experimental technique capable to do so in the way we discussed, but different experimental methods could be used to identify the ratio of bound to broken molecules (e.g., mass spectrometry) or the existence of different vibrational states (e.g., IR spectroscopy). There are also methods, namely pump-probe experiments, that grant access to the info more directly. The fact that we had 1000 molecules is not particularly relevant....

If in the coupling equations we can know the probabilities of electrons being in each electronic state by calculating the modulus squared of the coefficients $C_{1,2}(R,t)$, how can we know the probability/population of dissociated molecules? Can the sum of the probabilities of C_1 and C_2 be less than 1, meaning the rest is the dissociated molecules?

The sum over states and integral over R of the C_1 and C_2 will ALWAYS be 1 - unless we “loose” electrons or nuclei, something that rarely happens in experiments...in fact, never. If we define dissociated molecules as those whose distance is greater than a given threshold in a given electronic state (the ground state in the example discussed in class), then we can access the info on the dissociated fraction of molecules by looking at the integral of C_1 from the threshold to infinity. This is going to count the number of molecules that are in the ground state and with a nuclear distance greater than the dissociation distance.

In practice how do you estimate the error introduced by the use of approximations?

What approximations? For the classical nuclei, this is ok - at ambient conditions - for most systems, except H. For the B-O, it is typically the physics of the experiment that dictates the level of theory needed. E.g. if we model photochemistry we cannot use B-O. For the different ways to obtain potentials in the different types of molecular dynamics, ultimately it is comparison with experiments.

How do ML-based potentials compare to traditional force fields in terms of interpretability?

There is a loss of interpretability (though this is getting better) but a gain of accuracy and breadth of phenomena (e.g. ground state chemical reactions) that can be studied. We'll say a bit more about accuracy of the interactions in general in future classes.

I did not understand if this measurement of the bond lengths is achieved through an existing experimental technique, or if we consider that just in the context of this experiment, we are able to measure and assign to each individual particle a certain equilibrium bond length?

It was a thought experiment. I am not sure how we would measure bond lengths experimentally. We could certainly distinguish bound from dissociated (e.g. atomic mass spectroscopic) and frequencies associated to different vibrational states (ir spectroscopy).

Can the situation described during the lecture (2-level system undergoing photoexcitation) be treated using the Herzberg-Teller Franck-Condon approach, and/or what are the differences?

These two approaches refer to different treatments of the initial conditions on the excited states and - if I am not mistaken - vibronic couplings. The non-adiabatic dynamics that we are considering goes beyond that.

I couldn't understand how we could justify our assumption that upon excitation, our system was simply promoted to the excited electronic state such that $|c_2(R, \epsilon)\rangle = |c_1(R, 0)\rangle$.

This is called the Frank-Condon approximation. It builds on the idea that the photo excitation (for example, via a laser pulse) occurs "fast" on the time scale of motion of the nuclei and that is perfectly tuned to compensate for the energy difference between the ground and excited state. With these assumptions, the nuclei don't "move" during the pulse, but they acquire the energy needed to make the transition to the excited state.

During the lecture, you mentioned something about the Franck-Condon approximation. The Franck-Condon Principle states that the electronic transition takes place faster than the nuclei can respond. Why did we make this approximation?

The approximation simplifies the definition of the initial conditions for the propagation on the excited state and the subsequent non-adiabatic dynamics.

Also, is it related to the Born-Oppenheimer approximation?

Not really, what we are not taking into account here is mostly how the laser pulse affects the population as it excites it from the ground to the excited state.

In the BO approximation, we either assume that the system is completely in the ground state or the excited state. Now, if we want to actually study the light-matter interaction of, say, an atom or a qubit, what types of techniques are present? Will we be discussing them in the course?

Do you mean describing photon + matter together at the full quantum level? If so, beyond relatively simple model systems solvable analytically, there are some advanced (and in development) methods recently proposed by the group of Angel Rubio. He is not the only one tackling this problem, but the one I am more familiar with. These methods are - however - not covered in the course.

Is it possible to describe other excited states when treating the nuclei classically? Is there a way to describe the coupling between them?

Yes, some methods have been described in connection to the projects and will be explored in future lectures. The couplings are either modelled or computed using, for example the so-called time-dependent density functional theory or quantum chemistry methods.

Using AB INITIO MD we can compute the energy for a certain R and the goal is to have a good approximation but not computationally too expensive. Can we select "how many point" we want depending on the region of the plot? For example, we don't really care what happens at really short or really large R , but we need a more accurate approximation of the equilibrium of the non zero coupling distance so can we "guess" in which region we'll need more calculation or point ?

As we shall see better in future classes, the energy is computed only at the configurations visited along the trajectory. Good point, however.

As far as I understood from the lecture, the excited particle cannot return to the ground state, unless it is in the interaction area (since the interaction coefficients are negligible). Is that correct? If yes, why would a higher energy particle not be able to release the excess energy and return to the ground state at any point, instead of only in the interaction area?

The electrons do not see the additional energy that has brought them to the excited state as “excess” energy: it is additional energy that they have gained via the laser. This energy cannot be “changed” if there are no couplings in the evolution equation that trigger release - transfer from the excited to the ground state - or acquisition - transfer from the ground to the excited state. It is the total energy of the system, i.e. the average over the energy on the two states weighted by the probability to be in each one of them, that is conserved.

What is the final state of the two-level system with an initial condition in the excited state? After a sufficiently long period of evolution, will $c_2(R, t)$ eventually approach 0? And what will $c_1(R, t)$ become?

After a sufficient amount of time, the system reaches what is called a stationary state. In this condition, the amount of population gained and lost by each state in a given time is constant and so become the populations. The stationary values are not necessarily zero, this depends on the details of the surfaces and couplings.

Can we include the initial excitation pulse into the Coupled-Channel equation? For example, use an extra Hamiltonian to characterize the pulse?

Yes, this is done in “advanced” versions of the approach for example when describing the photochemistry of atmospheric molecules. The extension of the theory goes in the direction you indicate (extra term in the Hamiltonian) of by introducing an appropriate operator to describe the transition, e.g. matrix element of a “dipole”.

How do we calculate the couplings D_{12} ? How do we know in which regions are state transitions more likely to occur?

In fully quantum mechanical calculations, they are obtained via brute force solution of the time-independent Sch. equation for the electronic Hamiltonian. Once the eigenstates of the system are available the couplings are obtained by differentiation with respect to the nuclear positions. There is an alternative expression for the couplings that shows that they are inversely proportional to the energy gap between two states. This points to the fact that they are going to be large - and therefore promote transitions - in regions of close spacing of the electronic eigenvalues. In practice, these operators are either modelled or computed via approximations such as time-dependent density functional theory. More on this in future lectures.

We want to compute a system only in the ground state because it is computationally much easier to do. Is it possible to make an initial estimation on where the coupling terms are relevant, so that we know when our simulation enters this energetic region that the assumption of only working in the ground state is invalid?

Not really. However, typical energy gaps in the systems that we consider are of the order of several eVs, while the thermal energy of typical nuclei at room temperature is 0.025 eV. This means that it's quite hard to force nuclei outside the ground state without - say - a laser excitation. Also, the close energy regions among states where the non-adiabatic couplings become important are typically hard to reach (in the sense that they appear often at the top of an “energy barrier” in the ground state).

It was briefly mentioned during the lecture that population transfer between two states is possible. How can population transfer be calculated/quantified? Can the transition probability ever be greater than 50%? At which point can it be said that the B-O approximation fails? I'm guessing that such non-adiabatic behaviors will be relevant in some of the projects.

This was actually the core of the lecture ;-). The population transfer is computed by solving the equation for the coefficients and obtained via taking the integral of the modulus square of each one of them (which is the population on each state) at the various instants of time. The transfer can indeed be greater than 50%. The B-O approximation fails as soon as the population transfer is greater than zero, so no need to get to 1/2. Indeed, the projects on surface-hopping and Ehrenfest dynamics, in particular, focus on non-adiabatic dynamics.

Is the second-derivative term in the self-induced coefficient best interpreted as a diffusion-like operator, or does it have a fundamentally different role in quantum propagation?

The second derivative is the coordinate-representation of the kinetic energy operator in the Hamiltonian. This term represents the “free particle” motion of the system and you are correct in saying that it can be interpreted as a diffusion operator.

Additionally, if we introduce a third state into the system, is it sufficient to simply add another coupling term to the equations, or are there deeper structural changes required in the coupled-channel formulation?

Add one equation for the third coefficient and the corresponding coupling terms in all equations.

For the lecture, did we treat the total Hamiltonian of the system (electron + nuclei) time-dependent or independent? What about the electronic Hamiltonian? Also, do any of the Hamiltonians change when we perform the Franck-Condon approximation? Why? Why not?

The total Hamiltonian is time-independent.

What about the electronic Hamiltonian?

Also time independent. It is solved for each nuclear coordinate, but there is no explicit time dependency in any of the operators.

Also, does any of the Hamiltonians change when we perform the Franck-Condon approximation? Why? Why not?

No. We make the idealized hypothesis that the laser is instantaneous (i.e. switches on and off and transfers the population, but it never appears explicitly).